

$F(\text{Au}_2)$  and  $\nu(\text{Au}_2)$  values of 0.76 mdyn  $\text{\AA}^{-1}$  and 114  $\text{cm}^{-1}$ , respectively, not 185  $\text{cm}^{-1}$ . For  $\text{Au}_2(\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2)_2$ , the closest Raman feature is found at 138  $\text{cm}^{-1}$  and was attributed to a Au-S-C deformation on the basis of polarization data. These observations are consistent with those of Fackler, Clark, et al.,<sup>30</sup> and it appears that the  $\text{Au}_2(\text{S}_2\text{CNR}_2)_2$  spectra need to be reinvestigated.

The  $F(\text{Ag}_2)$  value for  $\text{Ag}_2(\text{dmpm})_2\text{Br}_2$  cannot be accurately obtained using conventional equations (diatomic model, valence force field expressions for linear X-M-M-X units<sup>33</sup>). The diatomic model suggests that  $F(\text{Ag}_2)$  would be 0.073 mdyn  $\text{\AA}^{-1}$ , while the valence force field equations cannot be solved.<sup>34</sup> In the former case, the presence of quasi-linearly bonded bromides ( $r(\text{AgBr}) = 2.74 \text{\AA}$ ) has been wrongly ignored. Nevertheless, the main conclusion from these simple calculations is that  $F(\text{Ag}_2)$  is indeed small. Vibrational and structural literature data for  $\text{Ag}_2$  compounds are scarce. Only four data points have been used (Table IX) in order to approximate a relationship similar to eq 3:

$$r(\text{Ag}_2) = -0.30 \ln F(\text{Ag}_2) + 2.5 \quad (4)$$

Using  $r(\text{Ag}_2) = 3.60 \text{\AA}$ , a value of 0.03 mdyn  $\text{\AA}^{-1}$  is calculated for  $F(\text{Ag}_2)$ . This value compares favorably with those listed in

- (33) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: New York, 1945; Vol. II, p 180.  
 (34) Assuming that the assignment for the Raman-active  $\nu(\text{AgBr})$  at 75  $\text{cm}^{-1}$  is correct (for the quasi-linear Br-Ag-Ag-Br moieties shown in structure I,  $r(\text{AgBr}) = 2.74 \text{\AA}$ ), the valence force field calculations for an X-M-M-X system (ignoring the presence of perpendicularly bonded phosphine and weakly bonded bromine ( $r(\text{AgBr}) = 2.9 \text{\AA}$ ) yield imaginary solutions.

Table VII and is consistent with the fact that for similar  $r(\text{M}_2)$  values (3.60  $\text{\AA}$  for  $\text{Ag}_2(\text{dmpm})_2\text{Br}_2$  and 3.54  $\text{\AA}$  for  $\text{Au}_2(\text{dmb})(\text{CN})_2$ ),  $F(\text{Ag}_2)$  should be smaller than  $F(\text{Au}_2)$ .<sup>35</sup>

**Acknowledgment.** This research was supported by the NSERC and FCAR. D.P. thanks the Université de Sherbrooke for an institutional graduate fellowship. W.P.S. and V.M.M. thank the NSF for Grant CHE-8219039 to purchase the diffractometer and the Exxon Educational Foundation for financial support. P.D.H. acknowledges Professor I. S. Butler (McGill University) for providing access to the Raman instruments and Mr. Y. Huang (McGill University) and Dr. Fran Adar (ISA) for technical assistance in the measurements of some of the Raman spectra.

**Registry No.**  $\text{Ag}_2(\text{dmpm})_2\text{Br}_2$ , 137945-44-9;  $[\text{Au}_2(\text{dmpm})_2](\text{PF}_6)_2$ , 137945-45-0;  $\text{Pd}_2(\text{dppm})_3$ , 37266-95-8;  $\text{Pt}_2(\text{dppm})_3$ , 37266-96-9;  $[\text{Ag}_2(\text{dppm})_3](\text{PF}_6)_2$ , 137964-62-6;  $[\text{Ag}_2(\text{dmpm})_2](\text{PF}_6)_2$ , 81343-14-8;  $\text{Pd}_2(\text{dmb})_2(\text{CN})_4$ , 137945-46-1;  $\text{Au}_2(\text{dmb})(\text{CN})_2$ , 124719-87-5;  $\text{Au}_2(\text{dmpm})_2\text{Cl}_2$ , 137945-47-2.

**Supplementary Material Available:** Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for  $\text{Ag}_2(\text{dmpm})_2\text{Br}_2$  and  $[\text{Au}_2(\text{dmpm})_2](\text{PF}_6)_2$  and a table showing a comparison between the Woodruff and reparametrized Herschbach-Laurie rules for  $\text{Au}_2$  compounds (5 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

- (35) (a) For the isostructural  $\text{M}_2(\text{dppm})_3$  complexes ( $\text{M} = \text{Pd}, \text{Pt}$ ) where  $r(\text{M}_2) \sim 3.0 \text{\AA}$ ,<sup>35b</sup> the  $F(\text{M}_2)$  values are 0.45 ( $\text{M} = \text{Pd}$ ) and 0.60 mdyn  $\text{\AA}^{-1}$  ( $\text{M} = \text{Pt}$ ).<sup>6a</sup> (b) Manojlovic-Muir, L. J.; Muir, K. W.; Grossel, M. C.; Brown, M. P.; Nelson, C. P.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* 1986, 1955. (c) Kirss, R. V.; Eisenberg, R. *Inorg. Chem.* 1989, 28, 3372.

Contribution from the Department of Chemistry,  
 Kent State University, Kent, Ohio 44242

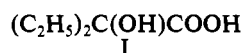
## Electron Transfer. 111. Disproportionation of Carboxylato-Bound Chromium(IV). Catalysis by Manganese(II)<sup>1</sup>

M. C. Ghosh,\* E. Gelerinter, and E. S. Gould\*

Received May 22, 1991

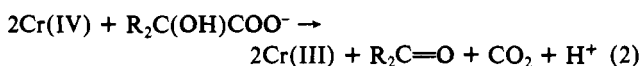
Tetrapositive chromium, Cr(IV), a state stabilized in aqueous solution through ligation by anions of branched  $\alpha$ -hydroxy acids, undergoes decay by a combination of disproportionation ( $2\text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}} + \text{Cr}^{\text{V}}$ ) and ligand oxidation. In solutions having pH 2.5-4.0, buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its anion ( $\text{Lig}^-$ ), disproportionation is very nearly quantitative and is found to be catalyzed markedly by Mn(II). Both the Cr(V) and Cr(III) products are bis chelates. In the absence of Mn(II), the disproportionation is second order in Cr(IV), and observed variation of rates with  $[\text{H}^+]$  and  $[\text{Lig}^-]$  points to a predominant reaction path entailing reactions of two units of the deprotonated complex,  $\text{Cr}^{\text{IV}}(\text{OH})$ , which species is also an important contributor to the Mn(II)-catalyzed reaction. For the latter, a nonlinear rate dependence on  $[\text{Mn}^{\text{II}}]$  indicates the formation of a Cr(IV)-Mn(II) adduct ( $K = 52$ ). Bridged precursor complexes are suggested for both the uncatalyzed ( $\text{Cr}^{\text{IV}}\text{-O-Cr}^{\text{IV}}$ ) and catalyzed ( $\text{Cr}^{\text{IV}}\text{-OH-Mn}^{\text{II}}$ ) reactions, and it is proposed that the catalyzed path involves a rate-determining conversion of Mn(II) to Mn(III), a state having a  $1e^-$  reduction potential near the gap between those for Cr(IV,III) and Cr(V,IV). In addition to this potential constraint, it is desirable that ligand substitutions about both states of the catalyst be more rapid than those about Cr(IV). Among the various  $1e^-$  redox couples derived from other d- and f-block metal centers, only Ce(IV,III) appears to conform to these requirements, but action in this case is complicated by preferential oxidation of the ligand by Ce(IV).

Both atypical oxidation states of chromium, Cr(V)<sup>2</sup> and Cr(IV),<sup>3</sup> may be stabilized in solution through chelation by anions of branched  $\alpha$ -hydroxy acids such as 2-ethyl-2-hydroxybutanoic acid (I). However, the two states are not equally persistent.



- (1) Sponsorship of this work by the National Science Foundation (Grant 9019840) is gratefully acknowledged.  
 (2) See, for example: (a) Krumpolc, M.; DeBoer, B. B.; Roček, J. *J. Am. Chem. Soc.* 1978, 100, 145. (b) Krumpolc, M.; Roček, J. *Ibid.* 1979, 101, 3206. (c) Gould, E. S. *Acc. Chem. Res.* 1986, 19, 66.  
 (3) (a) Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* 1990, 29, 4258. (b) *Ibid.* 1991, 30, 491.

Aqueous solutions of Cr(V), in the presence of an excess of the ligating anion, remain virtually unchanged in the dark at room temperature for up to 24 h, whereas Cr(IV) solutions, given comparable conditions, suffer perceptible loss within a few minutes. The latter state undergoes both disproportionation (eq 1) and

$$2\text{Cr}(\text{IV}) \rightarrow \text{Cr}(\text{III}) + \text{Cr}(\text{V}) \quad (1)$$


reduction by the parent ligand (eq 2) with the relative importance of these two modes of attrition dependent both on the acidity of the medium and on the nature and concentration of added transition-metal ions.

**Table I.** Stoichiometry of the Decomposition of Carboxylato-Bound Chromium(IV)

method	$10^3[\text{Cr}^{\text{IV}}]$ , M <sup>a</sup>	$10^3[\text{Mn}^{\text{II}}]$ , M	Cr <sup>V</sup> , % <sup>d</sup>	Cr <sup>III</sup> , % <sup>d</sup>
spectral <sup>b</sup>	10.0	0	42	
	4.5	0	43	
	7.0	30	48	
	4.0	30	46	
ESR	0.80	0	43	
	0.80	8.0	50	
ion exchange <sup>c</sup>	10.0	0		50

<sup>a</sup>Cr(IV) was generated by treatment of a known concentration of Cr(VI) with a 3-fold excess of As(III) in a solution 0.050 M each in 2-ethyl-2-hydroxybutanoic acid (I) and its sodium salt. <sup>b</sup>Calculated from measurements at 512 nm, using eq 3 in text. <sup>c</sup>Cr(III) product was eluted from anion-exchange resin with water after oxidation of Cr(V) with acidified BrO<sub>3</sub><sup>-</sup> (see Experimental Section). <sup>d</sup>Percent of chromium taken.

The present report describes the decomposition of Cr(IV) as generated by reduction of HCrO<sub>4</sub><sup>-</sup> with As(III)<sup>3b</sup> at pH 2.5–4.0, under which conditions disproportionation heavily predominates. This reaction is found to be catalyzed dramatically by Mn(II).

### Experimental Section

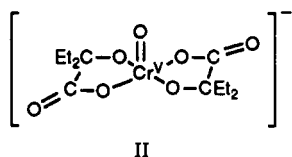
**Materials.** Sodium dichromate (MCB, reagent grade) and the "ligand acid" 2-ethyl-2-hydroxybutanoic acid (HLig, I) (Aldrich) were used as received. Solutions of As(III) were prepared by suspending reagent grade As<sub>2</sub>O<sub>3</sub> (Fisher) in water and then adding 1.0 M NaOH dropwise, with continuous stirring, until solution was complete. Solutions of Mn(II) were prepared by dissolving Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich) in 0.05 M HClO<sub>4</sub>. Solutions of NaClO<sub>4</sub> were prepared by neutralizing HClO<sub>4</sub> with NaHCO<sub>3</sub>. Chromium(IV) solutions were generated by treating 0.01 M As(III) in ligand buffer (HLig + Lig<sup>-</sup>) with a known deficiency of Cr(VI); in accord with the results of earlier work<sup>3b</sup> conversion of Cr(VI) to Cr(IV) was considered to be essentially complete after 30–200 s, depending upon [H<sup>+</sup>] and [Lig<sup>-</sup>].

**Stoichiometry.** The yields of Cr(V) in the Cr(V)–Cr(III) mixtures resulting from the decomposition of Cr(IV) were estimated both spectrophotometrically (at 512 nm) and from ESR measurements. In the former case, eq 3 was used, where [Cr]<sub>T</sub> is the total chromium taken and

$$\text{Abs}_{512} = \epsilon_5[\text{Cr}^{\text{V}}] + \epsilon_3([\text{Cr}]_{\text{T}} - [\text{Cr}^{\text{V}}]) \quad (3)$$

$\epsilon_5$  and  $\epsilon_3$  are the extinction coefficients of the two products (181 and 22 M<sup>-1</sup> cm<sup>-1</sup>) in the reaction medium.

For determination using ESR,<sup>4</sup> the intensity of the Cr(V) single-peak signal at  $g = 1.98$  was compared with those from known solutions of bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (complex II).<sup>5</sup>



II

To estimate Cr(III) in the presence of Cr(V), the reaction mixture was acidified to pH 0.95, and an excess of NaBrO<sub>3</sub> was added. The solution was allowed to stand for 1 h and was then subjected to anion-exchange chromatography (Dowex 1X2, 200–400 mesh, ClO<sub>4</sub><sup>-</sup> form). The green Cr(III) fraction was eluted with distilled water, and its Cr content was estimated by the method of Haupt.<sup>6</sup> The remaining Cr(VI) was slowly eluted from the resin with 1 M NaClO<sub>4</sub>.

Results are summarized in Table I.

**Examination of the Cr(III) Product.** The primary Cr(III) product, formed from the decomposition of 0.04 M Cr(IV) in a solution 0.3 M in both the ligating acid (HLig, I) and its anion (Lig<sup>-</sup>), was adsorbed on neither cation- nor anion-exchange resin, and as such, it could not be satisfactorily separated from the Cr(V) coproduct on either resin. Treatment of the acidified reaction mixture with BrO<sub>3</sub><sup>-</sup> (see preceding

section) converted Cr(V) to anionic HCrO<sub>4</sub><sup>-</sup>. Although oxidation of Cr(III) was negligible under the conditions used, some alteration of its ligand environment was evident, for the resulting separated green complex, which exhibited maxima at 574 ( $\epsilon_1 = 36$ ) and 411 nm ( $\epsilon_2 = 55 \text{ M}^{-1} \text{ cm}^{-1}$ ), was strongly adsorbed on polysulfonate resin, from which it could be eluted with 0.5 M NaClO<sub>4</sub>.

In separate experiments, the uncharged Cr(III) complex known to be formed from the Cr<sup>IV</sup>–(Mo<sup>V</sup>)<sub>2</sub> and the Cr<sup>V</sup>–ascorbate reactions<sup>3a,7</sup> in similarly buffered media was treated with BrO<sub>3</sub><sup>-</sup> under analogous conditions, yielding a Cr(III) species having spectral and elution characteristics corresponding to those indicated above.

**Kinetic Measurements.** Reactions were followed by measuring absorbance changes at 510 nm, employing either a Beckman Model 5260 or a Cary 14 recording spectrophotometer. In addition, the formation of Cr(V) could be monitored from the growth of its ESR signal, using an IBM ER 200D-SRC spectrometer. Solutions were buffered with measured quantities of the ligand acid, 2-ethyl-2-hydroxybutanoic acid (HLig, I), and its sodium salt (Na<sup>+</sup>Lig<sup>-</sup>). Ionic strength was regulated by addition of NaClO<sub>4</sub> solution. Reactions were initiated by adding the required quantity of Cr(VI) to a known excess of buffered As(III).

In the absence of added Mn(II), decay curves were nonexponential but corresponded closely to second-order profiles (eq 4). Treatment of data was in terms of observed absorbances ( $A_t$ ) and the initial and final values ( $A_0$  and  $A_\infty$ ) (eq 5).

$$1/[\text{Cr}^{\text{IV}}]_t - 1/[\text{Cr}^{\text{IV}}]_0 = kt \quad (4)$$

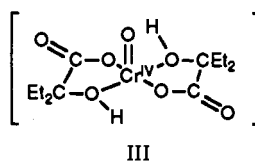
$$A_t = \frac{A_0 + A_\infty kt[\text{Cr}^{\text{IV}}]_0}{1 + kt[\text{Cr}^{\text{IV}}]_0} \quad (5)$$

Reactions were markedly accelerated by Mn(II). With [Mn<sup>II</sup>] > 0.010 M, reactions profiles were very nearly exponential, and pseudo-first-order specific rates could be estimated by using unweighted nonlinear least-squares fitting of data points to the relationship describing simple first-order transformations. At lower concentrations of Mn(II), decay patterns corresponded to a superposition of competing first- and second-order processes, and a somewhat more elaborate treatment of data (see Results and Discussion) was needed to obtain component specific rates.

The disproportionation of Cr(IV) was found to be unaffected by addition of the perchlorates or nitrates of Fe(III), Cu(II), Ni(II), Ag(I), La(III), and Tb(III) and by NH<sub>4</sub>VO<sub>3</sub> (each at the 0.003–0.01 M level). The loss of Cr(IV) was accelerated by addition of Ce(III); the latter reaction yielded Cr(III) but little Cr(V), suggesting that cerium (unlike manganese) catalyzes the reduction of Cr(IV) by the ligand present (reaction 2).

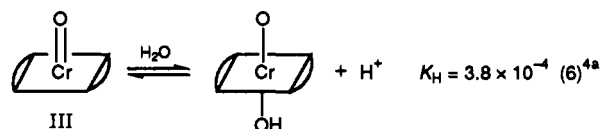
### Results

Previous reports<sup>3b,4a</sup> presented evidence that Cr(IV) in the buffer system used exists predominantly as the uncharged bis chelate

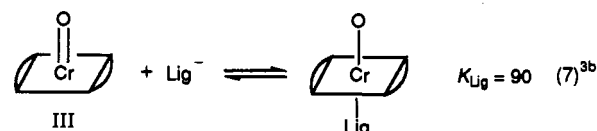


III

and that it undergoes partition between protonation levels



and between ligation levels



Both equilibria should be considered when the redox reactions at hand are treated.

The results of our stoichiometric experiments (Table I) indicate that under the conditions used Cr(IV) is converted to very nearly equivalent quantities of Cr(III) and Cr(V) whether or not Mn

(4) (a) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* 1985, 24, 4679. (b) Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* 1991, 30, 1039.  
(5) For ESR measurements in the presence of Mn(II), calibration of the Cr(V) signal was carried out with known concentrations of added Mn(II), since the Cr(V) peak was found to be broadened perceptibly by the d<sup>5</sup> center.  
(6) Haupt, G. W. *J. Res. Natl. Bur. Stand. Sect. A* 1952, 48, 41.

(7) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* 1987, 26, 2684.

**Table II.** Kinetic Data for the Uncatalyzed Disproportionation of Carboxylato-Bound Chromium(IV) ( $2 \text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}} + \text{Cr}^{\text{V}}$ )<sup>a</sup>

$10^4[\text{Cr}^{\text{IV}}]$ , M	$10^3[\text{As}^{\text{III}}]$ , M	$[\text{LigH}]$ , $\text{M}^b$	$[\text{Lig}^-]$ , $\text{M}^c$	pH	$k_{\text{obs}}$ , $\text{M}^{-1}$ $\text{s}^{-1}$ <sup>d</sup>
5.0	5.0	0.050	0.050	3.28	3.2 (2.9)
5.0	10.0	0.050	0.050	3.35	4.0 (3.6)
5.0	50.0	0.050	0.050	3.38	4.4 (4.0)
2.0	10.0	0.050	0.050	3.41	4.9 (4.5)
8.0	10.0	0.050	0.050	3.33	3.2 (3.3)
8.0	10.0	0.010	0.010	3.37	15.1 (18.3)
8.0	10.0	0.020	0.020	3.30	6.6 (8.4)
8.0	10.0	0.035	0.035	3.31	4.6 (4.7)
8.0	10.0	0.10	0.10	3.32	1.59 (1.47)
8.0	10.0	0.20	0.20	3.36	0.86 (0.92)
8.0	10.0	0.30	0.30	3.36	0.76 (0.60)
8.0	10.0	0.25	0.050	2.63	0.76 (0.78)
8.0	10.0	0.15	0.050	2.85	0.83 (0.83)
8.0	10.0	0.10	0.050	3.00	1.18 (1.17)
8.0	10.0	0.075	0.050	3.15	1.98 (1.82)
8.0	10.0	0.030	0.050	3.54	6.6 (7.0)
8.0	10.0	0.020	0.050	3.71	12.5 (12.1)
8.0 <sup>e</sup>	10.0	0.020	0.050	3.71	11.5 (12.1)
8.0	10.0	0.015	0.050	3.85	23 (20)
8.0	10.0	0.010	0.050	4.05	44 (35)

<sup>a</sup>Reactions were carried out at 25 °C,  $\mu = 0.50 \text{ M}$  ( $\text{NaClO}_4$ );  $\lambda = 510 \text{ nm}$ . <sup>b</sup>2-Ethyl-2-hydroxybutanoic acid (I). <sup>c</sup>2-Ethyl-2-hydroxybutanoate. <sup>d</sup>Second-order rate constants =  $(-d[\text{Cr}^{\text{IV}}]/dt)/[\text{Cr}^{\text{IV}}]^2$ ; parenthetical values were calculated from eq 8, using parameters in text. <sup>e</sup>Reaction was monitored using ESR (see Experimental Section).

is added. The spectrum of the Cr(V) product is that of the chelated  $\text{Cr}^{\text{V}}\text{O}$  anion (II).<sup>4a</sup>

The characteristics of the Cr(III) species remaining after oxidation of Cr(V) by  $\text{BrO}_3^-$  correspond to one of the products from reduction of the Cr(V) complex II with  $\text{Fe(II)}^8$  or  $\text{V(IV)}^8$ .<sup>4a</sup> Its elution behavior and visible spectra are those expected from a unipositive bis chelate.<sup>9</sup> This, however, is not the initially formed Cr(III) product, which is uncharged. The latter is taken to be a second bis chelate bearing an additional unidentate carboxylate group, a complex formed in the previously examined  $\text{Cr}^{\text{IV}}-(\text{Mo}^{\text{V}})_2$  and  $\text{Cr}^{\text{V}}-\text{ascorbate}$  systems.<sup>3a,7</sup> Partial aquation to our observed +1 complex (with loss of the pendant carboxylate but retention of the rings) has been shown to proceed under the oxidation conditions used.<sup>10</sup>

Kinetic data for the uncatalyzed bimolecular disproportionation of Cr(IV) appear in Table II. This reaction is seen to be inhibited by addition of the ligating anion,  $\text{Lig}^-$ , and, more markedly, by increases in acidity. Treatment of rate data is in terms of (8),

$$k_{\text{obs}} = \frac{k_1(K_{\text{H}})^2 + k_2(K_{\text{Lig}})^2[\text{H}^+]^2[\text{Lig}^-]^2}{(K_{\text{H}} + [\text{H}^+] + K_{\text{Lig}}[\text{H}^+][\text{Lig}^-])^2} \quad (8)$$

which is consistent with both the observed profiles and the known Cr(IV) equilibria, (6) and (7). The denominator of (8) reflects the partial conversion of Cr(IV) into "extraligated" species  $\text{Cr}^{\text{IV}}(\text{Lig})$  and the conjugate base  $\text{Cr}^{\text{IV}}(\text{OH})$ , whereas the numerator points to two kinetic paths, with the  $k_1$  component stemming from interaction of two units of  $\text{Cr}^{\text{IV}}(\text{OH})$  and the  $k_2$  term from reaction involving  $2 \text{Cr}^{\text{IV}}(\text{Lig})$ . Refinement of rates yields  $k_1 = 181 \pm 7 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = 0.71 \pm 0.06 \text{ M}^{-1} \text{ s}^{-1}$ . Table II also compares observed specific rates with those calculated using (8).<sup>11</sup> Note that the uncatalyzed disproportionation proceeds

(8) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(9) Spectral characteristics of a number of chelated and nonchelated (carboxylato)chromium(III) complexes have been summarized by Fanchiang.<sup>4a</sup>

(10) In addition we have noted<sup>3b</sup> that when Cr(IV) is allowed to decompose for 5 days at  $[\text{Lig}^-] = 0.1 \text{ M}$ , conversion to the tripositive state is complete, with 82% of the Cr(III) uncharged. Since this major fraction presumably includes the product from disproportionation of Cr(IV), as well as that from the (much slower) reduction of Cr(V) by the ligand acid, this observation corroborates our view that the principal Cr(III) product from the disproportionation is uncharged. This fraction ( $\epsilon_{587} = 48$ ;  $\epsilon_{427} = 57$ ) is also converted to the +1-charged bis chelate on treatment with acidified  $\text{BrO}_3^-$ .

**Table III.** Kinetic Data for the Mn(II) Catalysis of the Disproportionation of Cr(IV): Variation of [Catalyst]<sup>a</sup>

$10^3[\text{Mn}^{\text{II}}]$ , M	$10^4 k_c$ , $\text{s}^{-1}$ <sup>b</sup>	$10^4(k_c)_{\text{calcd}}$ , $\text{s}^{-1}$ <sup>c</sup>	$k_u$ , $\text{M}^{-1} \text{ s}^{-1}$ <sup>d</sup>
0.10	$0.50 \pm 0.12$	0.38	$4.4 \pm 0.1$
0.20	$0.86 \pm 0.20$	0.77	$4.1 \pm 0.1$
0.40	$1.33 \pm 0.20$	1.52	$4.4 \pm 0.1$
0.80	$3.1 \pm 0.1$	3.0	$3.9 \pm 0.1$
1.60	$5.1 \pm 0.1$	5.7	$3.9 \pm 0.1$
3.0	$9.3 \pm 0.2$	10.0	$4.3 \pm 0.1$
6.0	$18.1 \pm 0.1$	17.7	$3.9 \pm 0.1$
10.0	$27 \pm 1$	25	$4.3 \pm 0.2$
10.0 <sup>e</sup>	$25 \pm 1$	25	4.1 <sup>f</sup>
20.0	$38 \pm 1$	38	4.1 <sup>f</sup>

<sup>a</sup>Reactions were carried out at 25 °C,  $\mu = 0.50 \text{ M}$  ( $\text{NaClO}_4$ ); solutions were  $0.050 \text{ M}$  each in the ligand acid (I) and its anion; pH 3.30–3.38;  $[\text{Cr}^{\text{IV}}]_0 = 8.0 \times 10^{-4} \text{ M}$  throughout;  $\lambda = 510 \text{ nm}$ . <sup>b</sup>Specific rates for catalyzed disproportionation, obtained from treatment of kinetic data according to (10). <sup>c</sup>Values calculated from (11), using parameters in text. <sup>d</sup>Specific rates for uncatalyzed bimolecular path. <sup>e</sup>Values obtained from ESR data. <sup>f</sup>Values were kept invariant (at  $4.1 \text{ M}^{-1} \text{ s}^{-1}$ ) during these treatments.

preponderantly through "symmetric" transition states, i.e., those in which the two reacting partners are kinetically identical.

Of the added d- and f-block metal species examined, only Mn(II) was found to catalyze the Cr(IV) disproportionation significantly. At  $[\text{Mn(II)}] > 0.010 \text{ M}$ , the predominance of the catalyzed path leads to kinetic curves which are nearly exponential, implying a first-order dependence on  $[\text{Cr}^{\text{IV}}]$ . At lower values of  $[\text{Mn}^{\text{II}}]$ , profiles clearly reflect the competition between the catalyzed ( $k_c$ ) and uncatalyzed ( $k_u$ ) contributions (eq 9). Integration

$$\frac{-d[\text{Cr}^{\text{IV}}]}{dt} = k_c[\text{Cr}^{\text{IV}}] + k_u[\text{Cr}^{\text{IV}}]^2 \quad (9)$$

of (9), expression of concentrations in terms of absorbances ( $A$  values), and rearrangement of terms gives (10), where  $\Delta\epsilon = (A_0 - A_\infty)/[\text{Cr}^{\text{IV}}]_0$ .

$$A_t = \frac{[e^{k_c t}(k_u A_\infty^2 - k_c \Delta\epsilon A_\infty - k_u A_0 A_\infty) + A_\infty(k_c \Delta\epsilon + k_u A_0 - k_u A_\infty) - k_c A_0 \Delta\epsilon]}{[e^{k_c t}(k_u A_\infty - k_c \Delta\epsilon - k_u A_0) + k_u(A_0 - A_\infty)]} \quad (10)$$

Treatment of kinetic data for a series of runs in which  $[\text{Mn}^{\text{II}}]$  was varied yields kinetic components listed in Table III.<sup>12,13</sup> At low concentrations of catalyst, catalyzed rates are seen to be nearly proportional to  $[\text{Mn}^{\text{II}}]$ , but at higher concentrations, dependency becomes perceptibly less steep than that corresponding to unit order. This modest departure from linearity is consistent with the formation of a weakly associated Cr(IV)–Mn(II) complex, allowing the catalyzed reaction rate to be expressed as (11). Refinement in terms of (11) yields  $K$  (the  $\text{Cr}^{\text{IV}}-\text{Mn}^{\text{II}}$  association

(11) Inclusion of additional terms reflecting further bimolecular interactions between Cr(IV) species present (such as  $\text{Cr}^{\text{IV}}(\text{OH}) + \text{Cr}^{\text{IV}}(\text{Lig})$ ) did not significantly improve the agreement between observed and calculated rate constants.

(12) As an alternative to treating of our kinetic curves in terms of the relatively cumbersome expression (10), we utilized a numerical integration technique analogous to that described by Bose.<sup>13</sup> Application of a fourth-order Runge–Kutta integration procedure to (9) produced curves that were compared to observed profiles. Variation of  $k_c$  and  $k_u$  to achieve optimal agreement yielded specific rates essentially the same as those obtained by "closed-form" integration (as listed in Table III).

(13) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349.

(14) The observed variation of  $k_c$  with  $[\text{Mn}^{\text{II}}]$  is also consistent with partial conversion to a di- or polynuclear species analogous to those reported in alkoxy<sup>15</sup> and carboxylate-bound<sup>16</sup> systems. In addition, dimeric complexes of Mn(III) featuring the carboxylate ligand in the present study have been described.<sup>17</sup> However, on examining the spectra of Mn(II)–carboxylate mixtures under our kinetic conditions, we find no irregularities attributable to such polyions.

(15) (a) Murray, B. D.; Hope, H.; Power, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 169. (b) Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1863.

(16) Rardin, R. L.; Bino, A.; Poganiuch, P.; Tolman, W. B.; Liu, S.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 812.

(17) Saadeh, S. M.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 8.

$$k_c = \frac{-d[\text{Cr}^{\text{IV}}]/dt}{[\text{Cr}^{\text{IV}}]} = \frac{kK[\text{Mn}^{\text{II}}]}{1 + K[\text{Mn}^{\text{II}}]} \quad (11)$$

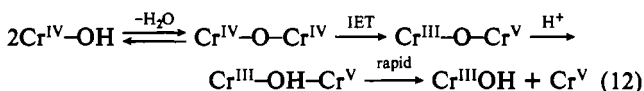
quotient) =  $52 \pm 11 \text{ M}^{-1}$  and  $k$  (the limiting rate at high  $\text{Mn}^{\text{II}}$ ) =  $(7.3 \pm 1.4) \times 10^{-3} \text{ s}^{-1}$ .<sup>14-17</sup>

The catalytic component is noticeably inhibited by increases in  $[\text{H}^+]$  and  $[\text{Lig}^-]$ . Typically, at 0.010 M  $\text{Mn}^{\text{II}}$ , the catalyzed rate is found to suffer a 50% decrease when the pH falls from 3.7 to 2.5 and a similar decrement occurs when  $[\text{Lig}^-]$  is increased from 0.02 to 0.30 M. These variations indicate that  $\text{Cr}^{\text{IV}}(\text{OH})$  is a somewhat more active species than either  $\text{Cr}^{\text{IV}}(\text{H}_2\text{O})$  or  $\text{Cr}^{\text{IV}}(\text{Lig})$ . However, the slight magnitude of these trends, in conjunction with the limited precision of our  $k_c$  values, appears to rule out evaluation of individual contributions of the three  $\text{Cr}(\text{IV})$  species to the catalyzed path.

### Discussion

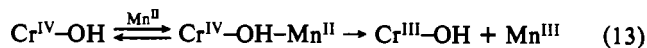
Our evidence that the primary  $\text{Cr}(\text{V})$  and  $\text{Cr}(\text{III})$  products are bis chelates (although the latter is not a thermodynamically favored species) is in accord with the earlier assignment of a bis-chelated structure to the predominant  $\text{Cr}(\text{IV})$  complex.<sup>3b</sup> The reactions at hand appear to proceed without disruption of the chelate rings.

A salient feature of the present study is the prominence of the kinetic term involving  $\text{Cr}^{\text{IV}}(\text{OH})$  in the uncatalyzed component, in addition to our evidence for the superior reactivity of this species in the catalyzed path as well, suggesting, but not demanding, an important inner-sphere contribution to both. We propose sequence (12) as the predominant route for the uncatalyzed disproportionation with the step entailing internal electron transfer (IET) rate-determining. For the rapid follow-up step, dissociation of the  $\text{Cr}(\text{III},\text{V})$  "successor complex", we favor breakage of the  $\text{Cr}^{\text{V}}\text{-O}$  bond in accord with the recognized greater substitution lability at the  $d^1$  center.<sup>18</sup>



tionation with the step entailing internal electron transfer (IET) rate-determining. For the rapid follow-up step, dissociation of the  $\text{Cr}(\text{III},\text{V})$  "successor complex", we favor breakage of the  $\text{Cr}^{\text{V}}\text{-O}$  bond in accord with the recognized greater substitution lability at the  $d^1$  center.<sup>18</sup>

Although the effective "bimolecular specific rate" ( $0.4 \text{ M}^{-1} \text{ s}^{-1}$ ) for the  $\text{Mn}(\text{II})$ -catalyzed conversion falls well below that for the reaction involving 2  $\text{Cr}^{\text{IV}}\text{OH}$ ,  $\text{Mn}(\text{II})$  catalysis assumes importance (and may predominate) at high  $[\text{Mn}(\text{II})]$  and low  $[\text{Cr}(\text{IV})]$ . This component almost certainly proceeds through  $\text{Mn}(\text{III})$ , i.e., via sequence (13) and (14). We suggest that internal electron transfer



within the  $\text{Cr}^{\text{IV}}(\text{OH})\text{Mn}^{\text{II}}$  precursor is slower than that within  $\text{Cr}^{\text{IV}}(\text{OH})\text{Mn}^{\text{III}}$ , for if (13) were the more rapid step, the growth of the  $\text{Cr}(\text{V})$  would not correspond to the loss of  $\text{Cr}(\text{IV})$ .

The catalytic effectiveness of  $\text{Mn}(\text{II})$  may then be attributed to the ease with which it undergoes  $\text{e}^-$  oxidation to a state having a reduction potential lying within or near the gap between those for  $\text{Cr}(\text{IV},\text{III})$  and  $\text{Cr}(\text{V},\text{IV})$ .<sup>19-24</sup> If, as we suspect, steps (13) and (14) proceed through  $\text{OH}$ -bridged intermediates, it is further advantageous that ligand substitutions about both  $\text{Mn}(\text{II})$  and  $\text{Mn}(\text{III})$  centers proceed more rapidly than those about  $\text{Cr}(\text{IV})$ .<sup>24</sup> In contrast, the couples  $\text{Ti}(\text{IV},\text{III})$ ,  $\text{V}(\text{V},\text{IV})$ , and  $\text{Fe}(\text{III},\text{II})$  are without catalytic action, presumably because the higher state in each case is too weakly oxidizing to convert  $\text{Cr}(\text{IV})$  to  $\text{Cr}(\text{V})$ . Catalysis by  $\text{Co}(\text{III},\text{II})$  is strongly disfavored by the very low rate of substitution characterizing the tripositive state, a difficulty which extends to very nearly all couples involving second- and third-row transition-metal centers where one or both states partaking in single-electron transactions is likely to be substitution inert. Elsewhere in the periodic table, the  $\text{Ce}(\text{IV},\text{III})$  couple appears to meet the requirements for catalysis, both with respect to its potential and to its substitution lability. However, its action is found to be complicated by the preferential oxidation, by  $\text{Ce}(\text{IV})$ , of the ligand in our medium, possibly reflecting the ease with which this tetrapositive lanthanide undergoes chelation with  $\alpha$ -hydroxy carboxylic acids.<sup>25</sup>

**Acknowledgment.** We thank Ms. Arla McPherson for technical assistance.

(18) See, for example: Bramley, R.; Ji, J.-Y.; Lay, P. A. *Inorg. Chem.* **1991**, *30*, 1557.

- (19) Formal potentials for  $\text{Cr}(\text{VI},\text{V})$  and  $\text{Cr}(\text{V},\text{IV})$  have been estimated<sup>20</sup> as 0.60 and 1.39 V, values which have been critically considered by Linck.<sup>21</sup> These potentials, in conjunction with the value 1.20 V for  $\text{Cr}(\text{VI},\text{III})$ ,<sup>22</sup> lead to a formal potential of 1.61 V for  $\text{Cr}(\text{IV},\text{III})$ . The  $E^\circ$  value for  $\text{Mn}(\text{III},\text{II})$  has been estimated as 1.50 V by Ciavatta.<sup>23</sup> Note that these values apply to 1 M  $\text{H}^+$ ; each is expected to be pH-dependent, but the dependencies may not conform to a single pattern. However, the observed catalysis by  $\text{Mn}(\text{II})$  of the  $\text{Cr}(\text{IV})$  disproportionation indicates that the trend in reduction potentials,  $\text{Cr}(\text{IV}) > \text{Mn}(\text{III}) > \text{Cr}(\text{V})$ , pertains to our media, as well as to pH 0.
- (20) Csanyi, L. J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1972; Vol. 7, p 510.
- (21) Linck, R. G. *Int. Rev. Sci.: Inorg. Chem., Ser. 2* **1974**, *9*, 191.
- (22) Beattie, J. K.; Haight, G. P. *Prog. Inorg. Chem.* **1972**, *17*, 97.
- (23) Ciavatta, L.; Grimaldi, M. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3071.
- (24) For kinetic studies of substitution reactions at  $\text{Mn}(\text{III})$  centers, see: (a) Adamson, A. W.; Welker, J. P.; Wright, W. B. *J. Am. Chem. Soc.* **1951**, *73*, 4786. (b) Fay, R. C.; Piper, T. S. *Ibid.* **1963**, *85*, 500.
- (25) See, for example: (a) Krishna, B.; Tewari, K. C. *J. Chem. Soc.* **1961**, 3097. (b) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 208.